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Singular perturbation refinement to quasi-steady state approximation in chemical kinetics†

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Abstract—It is shown that the well known quasi steady-state approximation of chemical reaction kinetics can be refined in a rigorous manner by the use of a powerful mathematical technique known as the method of singular perturbations. For the purpose of bringing out the essential features of this technique four typical kinetic schemes are analysed, namely those of reactions:
$R \rightarrow I \rightarrow P$; $R \leftrightarrows I \leftrightarrows P$; $R \rightarrow I$; $2I \leftrightarrows P$; and $R + M \leftrightarrows I + P + M$; $R + I \rightarrow P$; the latter corresponding to the case of thermal decomposition of ozone.

INTRODUCTION

THE "quasi-steady state approximation" (hereafter abbreviated Q.S.S.A.) for the reactive intermediate species, first introduced by BODENSTEIN and LUTKEMEYER [1], has generally led to essential simplifications in the differential equations which describe the instantaneous behaviour of reacting chemical species. In many cases, the use of this approximation has resulted in closed form analytical solutions for kinetic schemes which otherwise are mathematically tractable only by numerical techniques. The criteria for employing the Q.S.S.A. have been that both the concentration of the intermediate species and the relaxation time for approach to the "quasi-steady state concentration" (hereafter referred to as Q.S.S.C.) be small.

The regime of applicability of this assumption and the error resulting from its utilization have been considered by several authors [2–6]. The most notable efforts have been those of BENSON [2] and of GIDDINGS and SHIN [5]. The former obtained, for simple kinetic schemes, analytical solutions for the deviation of the reactive intermediate concentration from the Q.S.S.C. and sought by general considerations to extend his results to more complex systems; whereas the latter endeavoured to improve upon the Q.S.S.A. by what they termed a small perturbation solution of the mathematical equations.

As this paper is written to clarify several critical aspects of GIDDINGS and SHIN's analysis, the key feature of their work will now be briefly considered. After introducing an equilibrium departure term ε defined by

$$[I] = [I]^*(1 + \varepsilon) \tag{1}$$

where [I] and [I]* are respectively the actual concentration and the Q.S.S.C. of the intermediate species, GIDDINGS and SHIN derive a differential equation for ε, assumed small, by substituting equation (1) into the rate expression for the reactive intermediate and neglecting all the non-linear terms in ε. Since, however, it is usually postulated that initially [I] is zero, GIDDINGS and SHIN's analysis requires that $\varepsilon = -1$ at time $t = 0$, and thus, a parameter normally considered small is forced to be of order unity at small times. But a more serious objection, which also applies to the analysis of HIRSCHFELDER [6] and which will be considered in more detail later on, is that a consistently developed perturbation solution based upon the Q.S.S.A. cannot in general yield higher order terms (in this case ε) which will satisfy an arbitrary initial condition. One must then conclude that the satisfactory results demonstrated by GIDDINGS and SHIN may be fortuitous and that an adequate approximation to the exact solution may not necessarily result from

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applying their method to more complex kinetic schemes.

The purpose of this paper is then to clarify, in a more mathematically consistent manner, the nature and consequence of the Q.S.S.A. and to develop a rigorous scheme for generating higher-order terms to the solution of kinetic equations.

AN OUTLINE OF THE SINGULAR PERTURBATION METHOD

In order to illustrate our method of attack we shall now discuss at some length the very simple reaction scheme

$$R \xrightarrow{k_1} I$$

$$I \xrightarrow{k_2} P$$

in which both kinetic steps are first order.

Let

$$\lambda \equiv \frac{k_2}{k_1}, \quad \hat{y}_1 \equiv \frac{[R]}{[R]_0}, \quad \hat{y}_2 \equiv \frac{\lambda[I]}{[R]_0}, \quad \tau \equiv k_1 t$$

Then, the appropriate differential equations are

$$\frac{d\hat{y}_1}{dt} = -\hat{y}_1 \qquad \hat{y}_1(0) = 1 \tag{2}$$

$$\frac{1}{\lambda}\frac{d\hat{y}_2}{d\tau} = \hat{y}_1 - \hat{y}_2 \qquad \hat{y}_2(0) = 0 \tag{3}$$

the exact solutions to which, y_1 and y_2 respectively, are well known

$$\hat{y}_1 = \exp(-\tau)$$

and

$$\hat{y}_2 = \frac{\lambda}{\lambda - 1}[\exp(-\tau) - \exp(-\lambda\tau)] \qquad \lambda \neq 1$$

or

$$\hat{y}_2 = \tau \exp(-\tau) \qquad \lambda = 1$$

For purposes of illustration, however, we shall now attempt to construct the function $\hat{y}_2$ without referring to the exact solution. In particular it is clear from equation (3) that when $\lambda \to \infty$, and unless $d\hat{y}_2/d\tau$ also becomes infinite

$$\overset{(0)}{y}_2 = \hat{y}_1 = \exp(-\tau)$$

where, aside from the multiplying factor $\lambda/[R]_0$, $\overset{(0)}{y}_2$ obviously corresponds to the Q.S.S.C. of the reactive intermediate. Now, a natural development would be to generate correction terms to the Q.S.S.C. by means of a series solution in inverse powers of λ of the form

$$y_2(\tau) = \sum_{n=0}^{\infty} \frac{\overset{(n)}{y}_2(\tau)}{\lambda^n}$$

In this manner, equations for each of the perturbation functions $\overset{(n)}{y}_2(\tau)$ can be easily derived by substituting the series into equation (3) and then equating terms of equal powers in λ. There results

$$\overset{(0)}{y}_2 = \exp(-\tau)$$

$$\frac{d\overset{(n-1)}{y}_2}{d\tau} = -\overset{(n)}{y}_2 \qquad \text{for } n \geqslant 1$$

from which it readily follows that

$$\overset{(n)}{y}_2 = \exp(-\tau)$$

so that

$$y_2 = \exp(-\tau)\left\{1 + \frac{1}{\lambda} + \frac{1}{\lambda^2} + \ldots\right\}$$

$$= \frac{1}{1 - (1/\lambda)}\exp(-\tau) \tag{4}$$

It is immediately apparent now that the solution given by equation (4) does not contain adjustable constants and cannot therefore be made to satisfy the initial condition. This result is of course not surprising since the functions $\overset{(n)}{y}_2$ were obtained from algebraic rather than differential equations. Actually, the method of solution presented above will cease to apply for values of τ sufficiently close to zero no matter how large the magnitude of λ, since clearly even for $\lambda \to \infty$ there must exist a small but finite "relaxation" time interval where $\hat{y}_2$ will quickly rise from its initial zero value to the Q.S.S.C. Thus the term

$$\frac{1}{\lambda}\frac{d\hat{y}_2}{d\tau}$$

in equation (3) which to a first approximation was neglected, must obviously become at least as important as the other two terms for $\tau \sim 0$. It

becomes necessary therefore to develop, for $\tau \ll 1$, a different solution to equation (3) which will satisfy the initial conditions and which, as τ increases, will join smoothly with the function y_2 given by equation (4).

To arrive at this solution, which we shall denote by Y_2, we first modify our co-ordinate system so that all terms of the differential equation (3) become of the same order of magnitude even in the limit $\lambda \to \infty$. The appropriate co-ordinate transformation is $\omega = \lambda\tau$, and therefore, since

$$y_1 = \exp(-\tau) = \exp(-\omega/\lambda)$$

$$\frac{dY_2}{d\omega} = \exp(-\omega/\lambda) - Y_2 \qquad (5)$$

The exact solution of equation (5) is once again

$$Y_2 = \frac{1}{1-(1/\lambda)}\{\exp(-\omega/\lambda) - \exp(-\omega)\} \qquad \lambda \neq 1$$

or

$$Y_2 = \omega \exp(-\omega) \qquad \lambda = 1$$

Now to continue in the same vein as in our earlier development, we shall seek a solution for Y_2 by a perturbation expansion of the form

$$Y_2 = \sum_{n=0}^{\infty} \frac{\overset{(n)}{Y_2}}{\lambda^n}$$

When this series is substituted into equation (5) and $\exp(-\omega/\lambda)$ is expanded in a Taylor's series there results

$$\frac{d\overset{(n)}{Y_2}}{d\omega} = (-1)^n \frac{\omega^n}{n!} - \overset{(n)}{Y_2} \qquad n \geqslant 0$$

Solutions for the first few perturbation functions, subject to the initial conditions $\overset{(n)}{Y}(0) = 0$ for $n \geqslant 0$, are

$$\overset{(0)}{Y_2} = 1 - \exp(-\omega)$$

$$\overset{(1)}{Y_2} = -(\omega - 1) - \exp(-\omega)$$

$$\overset{(2)}{Y_2} = \frac{\omega^2 - 2\omega + 2}{2} - \exp(-\omega)$$

and thus a solution valid for small values of time is

$$Y_2 = 1 - \exp(-\omega) - \frac{1}{\lambda}[\omega - 1 + \exp(-\omega)] +$$

$$+ \frac{1}{2\lambda^2}[\omega^2 - 2\omega + 2 - 2\exp(-\omega)] + 0\left(\frac{1}{\lambda^3}\right) \qquad (6)$$

Following now an established convention [7, 8], we shall refer to y_2 as the "outer" solution and to Y_2 as the "inner" solution; and since both represent different forms of the same function $\hat{y}_2$—the exact solution to equation (3)—we must require that y_2 for $\tau \to 0$ identically match Y_2 for $\omega \to \infty$. It is indeed true that, as will be presently demonstrated, this matching requirement is automatically satisfied for this simple example; but for mathematical problems of greater complexity the matching condition becomes indispensable since it allows us to evalute the arbitrary constants that often appear in both the "inner" and the "outer" solutions. This particular point will, however, be considered later in more detail.

From equation (4), expanding the exponential term with $\tau \equiv \omega/\lambda$

$$\lim_{\tau \to 0} y_2 = \left\{1 - \frac{\omega}{\lambda} + \frac{\omega^2}{2\lambda^2} - 0\left(\frac{1}{\lambda^3}\right)\right\} \times$$

$$\times \left\{1 + \frac{1}{\lambda} + \frac{1}{\lambda^2} + 0\left(\frac{1}{\lambda^3}\right)\right\}$$

which, by collecting terms of equal powers in λ, may be rearranged into

$$\lim_{\tau \to 0} y_2 = 1 + \frac{1}{\lambda}(1 - \omega) +$$

$$+ \frac{1}{\lambda^2}\left(\frac{\omega_2}{2} - \omega + 1\right) + 0\left(\frac{1}{\lambda^3}\right)$$

Similarly, from equation (6)

$$\lim_{\omega \to \infty} Y_2 = 1 + \frac{1}{\lambda}(1 - \omega) +$$

$$+ \frac{1}{\lambda^2}\left(\frac{\omega^2}{2} - \omega + 1\right) + 0\left(\frac{1}{\lambda^3}\right)$$

Thus the matching requirement is identically met for terms up to $0(1/\lambda^3)$, but as can easily be shown, the matching will still remain valid if additional

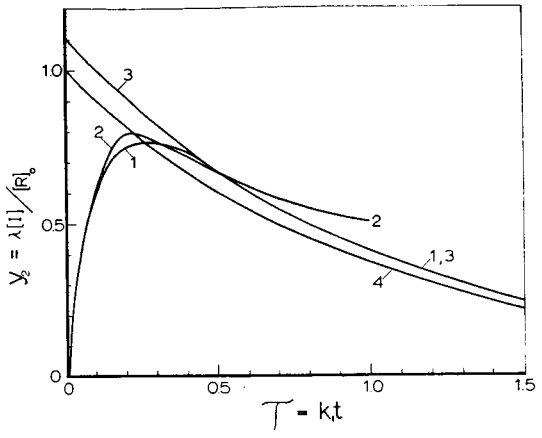

FIG. 1. History of concentration of intermediate species for the case of

$$R \overset{k_1}{\rightarrow} I \overset{k_2}{\rightarrow} P \quad \text{with} \quad \lambda \equiv k_2/k_1 = 10$$

1, exact solution, 2, inner solution up to $0(1/\lambda^3)$; 3, outer solution up to $0(1/\lambda^3)$; 4, Q.S.S.C.

terms in the two expansions are retained. Both inner and outer solutions are plotted along with the exact solution and the Q.S.S.C. in Fig. 1 for $\lambda = 10$.

The general form of the solutions to equation (3) is by no means merely an isolated phenomenon, but a behaviour common to a large variety of problems in mathematical physics. The distinguishing feature of our simple example has been of course that for large λ the exact solution could be approximated to any desired degree of accuracy by the "outer" solution y_2—which was derived from a straightforward perturbation expansion about the Q.S.S.A.—everywhere except for τ sufficiently small. Thus, a "boundary layer" phenomenon, so familiar to hydrodynamicists, was encountered in which the true solution $\hat{y}_2$ was found to change rapidly, over a short time interval of $0(1/\lambda)$, from a value given by equation (4) with $\tau \to 0$ to the prescribed initial condition. Such perturbation expansions, similar to the "outer" solution y_2 presented above, have been termed "singular", since they do not lead to a uniformly valid approximation to the true solution throughout the whole domain of interest, and the mathematical technique which has been developed for solving such equations, primarily in fluid mechanics [6–11], has become known as the "singular perturbation method". The examples which follow will, it is hoped, illustrate the steps of the singular perturbation technique more fully and show why it is ideally suited as an analytical tool for those problems in chemical kinetics for which the Q.S.S.A. ceases to be adequate and must therefore be refined.

The Usefulness of the Matching Requirement

Let us next consider a system with two simultaneous reversible first-order reactions

$$R \underset{k_1}{\overset{k_0}{\rightleftarrows}} I$$

$$I \underset{k_3}{\overset{k_2}{\rightleftarrows}} P$$

If

$$\hat{y}_1 \equiv \frac{[R]}{[R]_0}, \qquad \hat{y}_2 \equiv \frac{\lambda_2[I]}{[R]_0}$$

$$\hat{y}_3 \equiv \frac{[P]}{[R]_0}, \qquad \tau \equiv k_0 t,$$

$$\lambda_1 \equiv \frac{k_1}{k_0}, \qquad \lambda_2 \equiv \frac{k_2}{k_0}, \qquad \lambda_3 \equiv \frac{k_3}{k_0}$$

the differential equations are

$$\frac{d\hat{y}_1}{d\tau} = -\hat{y}_1 + \frac{\lambda_1}{\lambda_2}\hat{y}_2$$

$$\frac{1}{\lambda_2}\frac{d\hat{y}_2}{d\tau} = \lambda_3 C + (1-\lambda_3)\hat{y}_1 - \left(1 + \frac{\lambda_1}{\lambda_2} + \frac{\lambda_3}{\lambda_2}\right)\hat{y}_2$$

where the dimensionless concentration $\hat{y}_3$ has been eliminated by the mass-conservation relation

$$\hat{y}_1 + \frac{\hat{y}_2}{\lambda_2} + \hat{y}_3 = 1 + y_3^0 \equiv C$$

i.e. C is the value of the sum as $\tau \to 0$.

In order to examine the behaviour of the solution without any loss of generality let us consider a specific case where $\lambda_1 = 1$, $\lambda_3 = 2$, $C = 1$ while leaving $\lambda_2 \equiv \lambda$ as the perturbation parameter. The differential equations to be solved are then

$$\frac{d\hat{y}_1}{d\tau} = -\hat{y}_1 + \frac{1}{\lambda}\hat{y}_2 \qquad \hat{y}_1(0) = 1 \qquad (7)$$

$$\frac{1}{\lambda}\frac{dy_2}{d\tau} = 2 - \hat{y}_1 - \left(1 + \frac{3}{\lambda}\right)\hat{y}_2 \qquad \hat{y}_2(0) = 0 \qquad (8)$$

It is now clear that, as the two equations are coupled both $\hat{y}_1$ and $\hat{y}_2$ must be expanded in perturbation series similar to those presented in the previous example. Thus, for the "outer" region

$$\frac{d\overset{(0)}{y_1}}{d\tau} = -\overset{(0)}{y_1}, \qquad \overset{(0)}{y_2} = 2 - \overset{(0)}{y_1}$$

$$\frac{d\overset{(n)}{y_1}}{d\tau} = -\overset{(n)}{y_1} + \overset{(n-1)}{y_2}, \qquad n \geqslant 1$$

$$\hat{y}_2 = -\overset{(n)}{y_1} - 3\overset{(n-1)}{y_2} - \frac{d\overset{(n-1)}{y_2}}{d\tau}, \qquad n \geqslant 1$$

whereas for the "inner" solutions Y_1 and Y_2

$$\frac{d\overset{(0)}{Y_1}}{d\omega} = 0$$

$$\frac{d\overset{(0)}{Y_2}}{d\omega} = 2 - \overset{(0)}{Y_1} - \overset{(0)}{Y_2}$$

$$\frac{d\overset{(1)}{Y_1}}{d\omega} = -\overset{(0)}{Y_1}$$

$$\frac{d\overset{(n)}{Y_1}}{d\omega} = -\overset{(n-1)}{Y_1} + \overset{(n-2)}{Y_2} \qquad n \geqslant 2$$

$$\frac{d\overset{(n)}{Y_2}}{d\omega} = -\overset{(n)}{Y_1} - \overset{(n)}{Y_2} - 3\overset{(n-1)}{Y_2} \qquad n \geqslant 1$$

It should be carefully noted at this point, however, that, in contrast to our first example, the complete form of the "outer" solution cannot be derived without the *a priori* knowledge of the "inner" solution. Thus, it would be incorrect to specify that $\overset{(0)}{y_1}(0) = 1$ and $\overset{(0)}{y_1}(0) = 0$ for $n \geq 1$, since, for the reasons stated earlier, it would be improper to assume that the "outer" solution can be retained for $\tau \ll 1$. It follows, therefore, that the "outer" solutions y_1 and y_2, as obtained by solving *differential equations* for $\overset{(n)}{y_1}$ and algebraic equations for $\overset{(n)}{y_2}$, must contain a set of undetermined constants which can be evaluated only from the matching requirement between the "inner" and the "outer" solutions. This is illustrated below.

For the "outer" solution we have:

$$y_1 = C_0 \exp(-\tau) + \frac{1}{\lambda}[2 - (C_0\tau - C_1)\exp(-\tau)] +$$
$$+ \frac{1}{\lambda^2}\left[-8 + \right.$$
$$\left. + \left\{C_0\tau\left(\frac{\tau}{2} + 2\right) - C_1\tau + C_2\right\}\exp(-\tau)\right] + 0\left(\frac{1}{\lambda^3}\right)$$

and

$$y_2 = 2 - C_0\exp(-\tau) +$$
$$+ \frac{1}{\lambda}[-8 + \{C_0(\tau + 2) - C_1\}\exp(-\tau)] +$$
$$+ \frac{1}{\lambda^2}\left[32 - \left\{C_0\left(\frac{\tau^2}{2} + 4\tau + 5\right) - C_1(\tau + 2) + \right.\right.$$
$$\left.\left. + C_2\right\}\exp(-\tau)\right] + 0\left(\frac{1}{\lambda^3}\right)$$

whereas, for the "inner" solution

$$Y_1 = 1 - \frac{1}{\lambda}\omega +$$
$$+ \frac{1}{\lambda^2}\left\{\frac{\omega^2}{2} + \omega - [1 - \exp(-\omega)]\right\} + 0\left(\frac{1}{\lambda^3}\right)$$

and

$$Y_2 = 1 - \exp(-\omega) +$$
$$+ \frac{1}{\lambda}[\omega - 4 + (3\omega + 4)\exp(-\omega)] +$$
$$+ \frac{1}{\lambda^2}\left[16 - 3\omega - \frac{\omega^2}{2} - \right.$$
$$\left. - \left(16 + 13\omega + \frac{9}{2}\omega^2\right)\exp(-\omega)\right] + 0\left(\frac{1}{\lambda^3}\right)$$

Now, with $\tau \equiv \omega/\lambda$

$$\lim_{\tau \to 0} y_1 = C_0 + \frac{1}{\lambda}[2 + C_1 - C_0\omega] +$$
$$+ \frac{1}{\lambda^2}\left[-8 + C_2 - \omega(C_0 + C_1) + \frac{\omega^2}{2}C_0\right] +$$
$$+ 0\left(\frac{1}{\lambda^3}\right)$$

$$\lim_{\tau\to 0} y_2 = 2 - C_0 +$$

$$+\frac{1}{\lambda}[2C_0 - 8 - C_1 + C_0\omega] +$$

$$+\frac{1}{\lambda^2}\left[32 - 5C_0 + 2C_1 - C_2 + \omega(C_1 - C_0) - \right.$$

$$\left. - \frac{C_0}{2}\omega^2\right] + 0\left(\frac{1}{\lambda^3}\right)$$

$$\lim_{\omega\to\infty} Y_1 = 1 - \frac{1}{\lambda}(\omega) +$$

$$+\frac{1}{\lambda^2}\left(\frac{\omega^2}{2} + \omega - 1\right) + 0\left(\frac{1}{\lambda^3}\right)$$

$$\lim_{\omega\to\infty} Y_2 = 1 + \frac{1}{\lambda}(-4 + \omega) +$$

$$+\frac{1}{\lambda^2}\left(16 - 3\omega - \frac{\omega^2}{2}\right)$$

from which it follows that the matching requirement is met identically for all terms up to $0(1/\lambda^3)$ if

$$C_0 = 1, \qquad C_1 = -2, \qquad C_2 = 7$$

Incidentally, the numerical values of these coefficients would of course have been different if one had required, incorrectly, that the "outer" solution y_1 should satisfy the initial condition at $\tau = 0$.

THE BREAKDOWN OF THE Q.S.S.A. FOR LARGE TIMES

Even though in the two cases so far considered it was found possible to develop the exact solution in terms of an "inner" and an "outer" solution, the latter based on the Q.S.S.A., it should not be erroneously inferred that for all possible kinetic schemes subjected to an identical treatment, one should always be able to approximate the exact solution by only two expansions, each valid over a well defined range of τ. As the next two examples will demonstrate, an additional expansion may be required, since the "outer" solution based on the Q.S.S.A. may, under certain conditions, break down at some finite value of τ. This may occur for the following reason. If one formally expresses the "outer" solution as

$$y_2 = \sum_{n=0}^{\infty} \frac{{}^{(n)}y_2}{\lambda^n}$$

one implicitly assumes of course that for λ sufficiently large

$${}^{(n)}y_2 \gg {}^{(n+1)}y_2/\lambda \qquad \text{for all } \tau \tag{9}$$

We have already shown, however, that equation (9) cannot hold for sufficiently small τ and it is reasonable to suppose that, perhaps, it may also fail for sufficiently large τ. This, in turn, would imply a breakdown of the Q.S.S.A. for both small and large τ. Unfortunately, since a set of rules for deriving a valid solution cannot be easily prescribed, each differential equation must be considered separately. The next two examples will illustrate the technique for circumventing this difficulty.

Consider the relatively simple scheme

$$\mathrm{R} \xrightarrow{k_1} \mathrm{I}$$

$$2\mathrm{I} \xrightarrow{k_2} \mathrm{P}$$

and let

$$\hat{y}_1 \equiv \frac{[\mathrm{R}]}{[\mathrm{R}]_0}, \qquad \hat{y}_2 \equiv \frac{\lambda[\mathrm{I}]}{[\mathrm{R}]_0},$$

$$\tau = k_1 t, \qquad \lambda = \sqrt{\left(\frac{k_2}{k_1}[\mathrm{R}]_0\right)}$$

Then the appropriate equations are

$$\left.\begin{aligned} \frac{d\hat{y}_1}{d\tau} &= -\hat{y}_1 \\ \frac{1}{\lambda}\frac{d\hat{y}_2}{d\tau} &= \hat{y}_1 - (\hat{y}_2)^2 \end{aligned}\right\} \tag{10}$$

and since for all τ

$$\hat{y}_1 = \exp(-\tau)$$

it follows that

$$\frac{1}{\lambda}\frac{d\hat{y}_2}{d\tau} = \exp(-\tau) - (\hat{y}_2)^2 \tag{11}$$

Although the solution to equation (11) may be obtained by standard methods [12] and is found to be

$$\hat{y}_2 = \frac{e^{-\tau/2}[\alpha K_1(2\lambda\, e^{-\tau/2}) - I_1(2\lambda\, e^{-\tau/2})]}{\alpha K_0(2\lambda\, e^{-\tau/2}) + I_0(2\lambda\, e^{-\tau/2})} \tag{11a}$$

where

$$\alpha \equiv \frac{I_1(2\lambda)}{K_1(2\lambda)}$$

and $I_p(x)$ and $K_p(x)$ are, respectively, modified Bessel's functions of the first and second kind of order p and with argument x [13], we shall, as in the previous two examples, develop an "outer" and "inner" perturbation expansion for this problem. We find by following our procedure that with the Q.S.S.A. as the leading term the "outer" solution is

$$y_2 = \exp\left(\frac{-\tau}{2}\right) + \frac{1}{4\lambda} - \frac{1}{32\lambda^2}\exp\left(\frac{\tau}{2}\right) + \frac{1}{64\lambda^3}\exp(\tau) + 0\left(\frac{1}{\lambda^4}\right)$$

while the "inner" solution is

$$Y_2 = \frac{1-\exp(-2\omega)}{1+\exp(-2\omega)} + \frac{1}{\lambda}\left[\frac{1}{1+\exp(-2\omega)}\right]^2 \times \left\{\frac{1}{4} - \frac{\omega}{2} - (\omega^2 + \tfrac{1}{2})\exp(-2\omega) + \left(\frac{\omega}{2} + \frac{1}{4}\right)\exp(-4\omega)\right\} + 0\left(\frac{1}{\lambda^2}\right)$$

We now perceive, however, that although as in the first example, the matching requirement is identically satisfied, the outer expansion ceases to represent a uniformly valid approximation to the exact solution when

$$\exp\left(\frac{-\tau}{2}\right) \sim \frac{1}{4\lambda}$$

or

$$\tau \sim 2\ln 4\lambda$$

Consequently, the Q.S.S.A. remains valid only as long as $\tau \ll 2\ln 4\lambda$. For larger τ, a third expansion must clearly be sought and matched to the outer solution as $\tau \to \infty$ if the behaviour of the reactive intermediate is to be correctly predicted for all τ. To establish this "far out" solution we seek a transformation of both the co-ordinate system and the dependent variable which will make the solution both independent of λ as $\lambda \to \infty$ and uniformly valid for all $\tau \gg 1$. This may be accomplished by setting

$$z = \lambda \hat{y}_2$$

and

$$\eta = \lambda^2 \exp(-\tau)$$

so that the differential equation for y_2 becomes

$$\frac{dz}{d\eta} - \frac{z^2}{\eta} + 1 = 0 \tag{12}$$

This is equivalent to equation (11) and in view of equation (11a)

$$z = \frac{-\eta\{CI_1(2\eta^{1/2}) + K_1(2\eta^{1/2})\}}{CI_0(2\eta^{1/2}) - K_0(2\eta^{1/2})} \tag{13}$$

For this very special case the "far out" solution, equation (13), could be made identical to the exact solution, equation (11a), but, in order to bring out more clearly the essential features of the singular perturbation technique, we shall determine the constant C by matching the "outer" solution y_2 as $\tau \to \infty$ to the "far out" solution z as $\eta \to \infty$.

Since

$$y_2 \to \exp(-\tau/2) \quad \text{as} \quad \tau \to \infty$$

this is equivalent to requiring that

$$z \to \eta^{1/2} \quad \text{as} \quad \eta \to \infty$$

Now, if we employ the well established asymptotic expansion [13] for I_0, I_1, K_0 and K_1, we find that

$$\lim_{\eta\to\infty} z = \frac{-\eta^{1/2}\{C + \pi\exp(-4\eta^{1/2})\}}{C - \pi\exp(-4\eta^{1/2})}$$

from which it clearly follows that the only permissible value for C is zero. Thus the appropriate "far out" solution for $\lambda \gg 1$ is

$$z = \lambda y_2 = \eta^{1/2}\frac{K_1(2\eta^{1/2})}{K_0(2\eta^{1/2})} \tag{13a}$$

which, it should be noted, does not contain λ explicity. The exact inner, outer and "far out" solutions are sketched in Fig. 2 for $\lambda = 10$.

It is fair to remark, however, that, in this particular case at any rate, the use of the Q.S.S.A. and the subdivision of the solution into three rather than two distinct forms is strictly speaking unnecessary. It can be easily verified that a straightforward perturbation expansion, with equation (13a) rather than the Q.S.S.A. as the first term, will yield a solution which is uniformly valid throughout the complete "outer" region. Thus, it may perhaps be somewhat artificial to speak of an "outer" and a "far out" solution, since both may be meshed

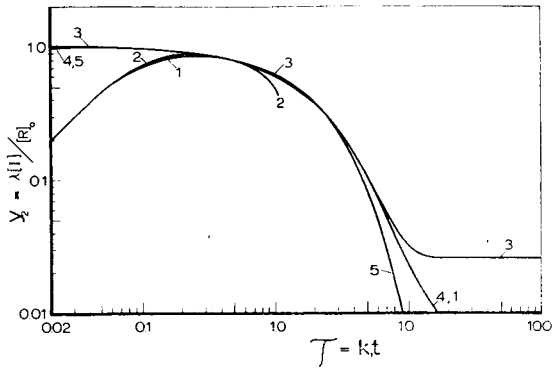

FIG. 2. History of concentration of intermediate species for the case of

$$R \xrightarrow{k_1} I; \quad 2I \xrightarrow{k_2} P \quad \text{with} \quad \lambda \equiv \sqrt{\left(\frac{k_2}{k_1}[R]_0\right)} = 10$$

1, exact solution; 2, inner solution up to $0(1/\lambda^2)$; 3, outer solution up to $0(1/\lambda^2)$; 4, "far out" solution up to $0(1/\lambda)$; 5, Q.S.S.C.

into a single function by a suitable transformation; but since a perturbation solution with the Q.S.S.A. as the first term can usually be constructed with ease and since the range of validity of this expansion does generally extend over the most important part of the "outer" region, there are obvious merits in retaining the technique presented above.

THE THERMAL DECOMPOSITION OF OZONE

The final example is the first application of our method to a kinetic scheme of a more practical importance, namely the thermal decomposition of ozone. If R is identified as an ozone molecule, I as an oxygen-atom and P as an oxygen molecule, the kineticist will quickly recognize the generally accepted decomposition scheme [14].

$$R + M \underset{k_2}{\overset{k_1}{\rightleftarrows}} I + P + M$$

$$R + I \xrightarrow{k_3} P$$

where M represents either an ozone, an oxygen or an inert molecule. To each of these molecules is ascribed an efficiency, not necessarily the same for the forward and back reaction, which accounts for the effectiveness of that molecule in causing the reaction to proceed. A case of interest to the kineticist is that of very dilute ozone–oxygen mixtures so that M may be replaced by P, which is assumed to have an efficiency of one half in the forward reaction and of one in the reverse reaction. Thus, if

$$\hat{y}_1 \equiv \frac{[R]}{[R]_0}, \qquad \hat{y}_2 \equiv \frac{\lambda[I]}{[R]_0},$$

$$\hat{y}_3 \equiv \frac{[P]}{[P]_0} \simeq 1, \qquad \lambda_1 \equiv 2\frac{k_2}{k_1}[P]_0,$$

$$\lambda \equiv 2\frac{k_3[R]_0}{k_1[P]_0}, \qquad \omega = \lambda\tau,$$

$$t \equiv \frac{k_1[P]_0 t}{2}$$

then the appropriate differential equations are

$$\frac{d\hat{y}_1}{d\tau} = -\hat{y}_1 - \hat{y}_1\hat{y}_2 + \frac{\lambda_1}{\lambda}\hat{y}_2 \tag{14}$$

$$\frac{1}{\lambda}\frac{d\hat{y}_2}{d\tau} = \hat{y}_1 - \hat{y}_1\hat{y}_2 - \frac{\lambda_1}{\lambda}\hat{y}_2 \tag{15}$$

Now, if as in the previous examples we introduce perturbation expansions for the "outer" and "inner" solutions, we can show that for the "outer" perturbation functions

$$n = 0 \quad \frac{d\overset{(0)}{y}_1}{d\tau} = -\overset{(0)}{y}_1 - \overset{(0)}{y}_1\overset{(0)}{y}_2$$

$$0 = \overset{(0)}{y}_1 - \overset{(0)}{y}_1\overset{(0)}{y}_2,$$

$$n = 1 \quad \frac{d\overset{(1)}{y}_1}{d\tau} = -\overset{(1)}{y}_1 - (\overset{(0)}{y}_1\overset{(1)}{y}_2 + \overset{(1)}{y}_1\overset{(0)}{y}_2) + \lambda_1\overset{(0)}{y}_2$$

$$\frac{d\overset{(0)}{y}_2}{d\tau} = \overset{(1)}{y}_1 - (\overset{(0)}{y}_1\overset{(1)}{y}_2 + \overset{(1)}{y}_1\overset{(0)}{y}_2) - \lambda_1\overset{(0)}{y}_2$$

$$\eta = 2 \quad \frac{d\overset{(2)}{y}_1}{d\tau} = -\overset{(2)}{y}_1 - (\overset{(0)}{y}_1\overset{(2)}{y}_2 + \overset{(2)}{y}_1\overset{(0)}{y}_2) - \overset{(1)}{y}_1\overset{(1)}{y}_2 + \lambda_1\overset{(1)}{y}_2$$

$$\frac{d\overset{(1)}{y}_2}{d\tau} = \overset{(2)}{y}_1 - (\overset{(0)}{y}_1\overset{(2)}{y}_2 + \overset{(2)}{y}_1\overset{(0)}{y}_2) - \overset{(1)}{y}_1\overset{(1)}{y}_2 - \lambda_1\overset{(1)}{y}_2$$

etc.

while for the "inner" perturbation functions

$$n=0 \quad \frac{d\overset{(0)}{Y_1}}{d\omega}=0, \qquad \overset{(0)}{Y_1}(0)=1$$

$$\frac{d\overset{(0)}{Y_2}}{d\omega}=\overset{(0)}{Y_1}-\overset{(0)}{Y_1}\overset{(0)}{Y_2}, \qquad \overset{(0)}{Y_2}(0)=0$$

$$n=1 \quad \frac{d\overset{(1)}{Y_1}}{d\omega}=-\overset{(0)}{Y_1}-\overset{(0)}{Y_1}\overset{(0)}{Y_2}, \qquad \overset{(1)}{Y_1}(0)=0$$

$$\frac{d\overset{(1)}{Y_2}}{d\omega}=\overset{(1)}{Y_1}-(\overset{(0)}{Y_1}\overset{(1)}{Y_2}+\overset{(1)}{Y_1}\overset{(0)}{Y_2})-$$

$$-\lambda_1\overset{(0)}{Y_2}, \qquad \overset{(1)}{Y_2}(0)=0$$

$$n=2 \quad \frac{d\overset{(2)}{Y_1}}{d\omega}=-\overset{(1)}{Y_1}-(\overset{(0)}{Y_1}\overset{(1)}{Y_2}+\overset{(1)}{Y_1}\overset{(0)}{Y_2})+$$

$$+\lambda_1\overset{(0)}{Y_2}, \qquad \overset{(2)}{Y_1}(0)=0$$

$$\frac{d\overset{(2)}{Y_2}}{d\omega}=\overset{(2)}{Y_1}-(\overset{(0)}{Y_1}\overset{(2)}{Y_2}+\overset{(2)}{Y_1}\overset{(0)}{Y_2})-$$

$$-\overset{(1)}{Y_1}\overset{(1)}{Y_2}-\lambda_1\overset{(1)}{Y_2}, \qquad \overset{(2)}{Y_2}(0)=0$$

etc. The "outer" solutions are

$$y_1=C_0\exp(-2\tau)+\frac{1}{\lambda}[\lambda_1+C_1\exp(-2\tau)]+$$

$$+\frac{1}{\lambda^2}\left[C_2\exp(-2\tau)-\frac{\lambda_1}{2C_0}\exp(2\tau)(\lambda_1+1)\right]+$$

$$+0\left(\frac{1}{\lambda^3}\right)$$

$$y_2=1-\frac{1}{\lambda}\left(\frac{\lambda_1}{C_0}\right)\exp(2\tau)+$$

$$+\frac{1}{\lambda^2}\left\{\frac{\lambda_1}{C_0^2}\exp(4\tau)[2\lambda_1+2+C_1\exp(-2\tau)]\right\}+$$

$$+0\left(\frac{1}{\lambda^3}\right)$$

while the inner solutions are

$$Y_1=1+\frac{1}{\lambda}[-2\omega+1-\exp(-\omega)]+$$

$$+\frac{1}{\lambda^2}[2\{\omega^2-\omega(1-\lambda_1)+1\}+$$

$$+\{-\omega^2+\omega(\lambda_1+1)-3-\exp(-\omega)\}$$

$$\exp(-\omega)]-\frac{1}{\lambda^2}3\lambda_1[1-\exp(-\omega)]+0\left(\frac{1}{\lambda^3}\right)$$

$$Y_2=1-\exp(-\omega)+\frac{1}{\lambda}(\{-\omega^2+\omega(\lambda_1+1)-$$

$$-1+\exp(-\omega)\}\exp(-\omega)-$$

$$-\lambda_1[1-\exp(-\omega)])+0\left(\frac{1}{\lambda^2}\right)$$

and these can be matched in the manner already described if

$$C_0=1, \qquad C_1=1-\lambda_1,$$

$$C_2=2+\frac{\lambda_1}{2}(\lambda_1-5)$$

Once again we observe, however, that as was the case with the previous example, the "outer" solution will break down when

$$\frac{\lambda_1}{\lambda C_0}\exp(2\tau)=\frac{\lambda_1}{\lambda}\exp(2\tau)\simeq 1$$

or

$$\tau\sim\tfrac{1}{2}\ln\left(\frac{\lambda}{\lambda_1}\right)$$

For the rate constants reported by BENSON and AXWORTHY [14] and a 5 m/o initial ozone concentration at 750°K and 1 atm oxygen this corresponds to

$$\tau\simeq 1{\cdot}7$$

Hence, since the Q.S.S.A becomes invalid for larger τ, another expansion must be sought for the "far out" region, which, as in the previous example, may be accomplished by a transformation of both τ and the dependent variables. Thus, with

$$\eta=\lambda\exp(-2\tau)$$

$$z_1=\lambda y_1, \qquad z_2=y_2$$

equations (14) and (15) are transformed into

$$\frac{dz_1}{d\eta}=\frac{z_1}{2\eta}(1+z_2)-\frac{\lambda_1}{2\eta}z_2 \tag{16}$$

$$\frac{dz_2}{d\eta}=-\frac{z_1}{2\eta}+\frac{z_2}{2\eta}(z_1+\lambda_1) \tag{17}$$

with the requirement that as $\eta \to \infty$, $z_1 \to \eta$, $z_2 \to 1$.

Equations (16) and (17) may next be integrated either numerically or by the method of successive approximations [15]. Thus, if in equation (16) z_2 is considered a function of η and, in equation (17), z_1, is taken as a function of η we can easily show that, formally,

$$z_1 = C\eta^{1/2} \exp\left(\int \frac{z_2}{2\eta}\, d\eta\right) + \\ + \lambda_1 \eta^{1/2} \exp\left(\int \frac{z_2}{2\eta}\, d\eta\right) \times \\ \times \int \left[\eta^{(-\lambda_1/2)} \frac{d}{d\eta}\left\{\exp\left(-\int \frac{z_2}{2\eta}\, d\eta\right)\right\}\right] d\eta \qquad (18)$$

and

$$z_2 = C_1 \eta^{(\lambda_1/2)} \exp\left(\int \frac{z_1}{2\eta}\, d\eta\right) + \\ + \eta^{(\lambda_1/2)} \exp\left(\int \frac{z_1}{2\eta}\, d\eta\right) \times \\ \times \int \left[\eta^{(-\lambda_1/2)} \frac{d}{d\eta}\left\{\exp\left(-\int \frac{z_1}{2\eta}\, d\eta\right)\right\}\right] d\eta \qquad (19)$$

in which the constants C and C_1 must be evaluated from the matching conditions that as $\eta \to \infty$, $z_1 \to \eta\, z_2, \to 1$.

This system may now be solved by letting $z_1 = \eta$ in equation (19) and noting that $C_1 = 0$ so that

$$z_2 = \frac{\eta^{\lambda_1/2} \exp(\eta/2)}{2} \int_\eta^\infty \beta^{-\lambda_1/2} \exp^{-\beta/2}\, d\beta$$

which may in turn be substituted into equation (18) to yield an improved approximation to z_1. The iteration can then be repeated until the desired accuracy is reached.

The solution just obtained will of course be accurate only up to terms of $0(1/\lambda)$ since it has been matched only to the first term of the "outer" solution. Additional terms may then be generated by a straight forward perturbation expansion which, as can easily be shown, will hold throughout the complete "outer" region. Thus, as in the previous section, it may be argued once again that perhaps the Q.S.S.A. and the resulting perturbation expansion may appear unnecessary since they can be replaced by a different solution which will be uniformly valid throughout the complete "outer" region. It is clear on the other hand though that, in contrast to this more general solution, the Q.S.S.A. has the great advantage of allowing us to construct an *analytic* solution, which although not valid for all $\tau > 0(1/\lambda)$ is at least applicable to that part of the "outer" region which is in general the one of most importance.

The solutions for the reactive intermediate in the three regimes are plotted in Fig. 3. Values of $\lambda_1 = 3{\cdot}0$ and $\lambda = 98$ correspond to those that may occur for dilute ozone decomposing isothermally at approximately 750°K.

CONCLUDING REMARKS

The examples which have been presented so far will, it is hoped, illustrate the power and versatility of the singular perturbation technique as applied to problems in chemical kinetics. It should be revealed in closing, however, that an expansion of the form

$$y = \sum_{n=0}^{\infty} \frac{y^{(n)}}{\lambda^n}$$

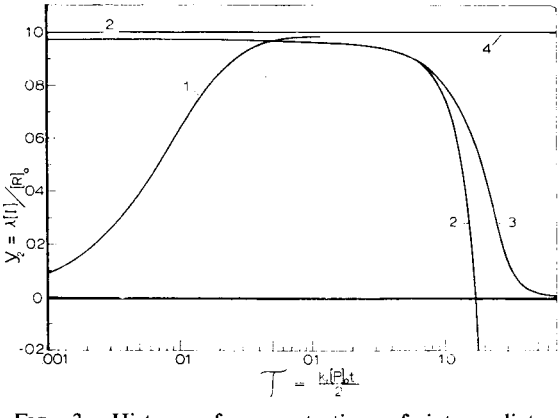

FIG. 3. History of concentration of intermediate species for the case of

$$R + M \underset{k_2}{\overset{1}{\rightleftarrows}} I + P + M; \quad R + I \xrightarrow{k_3} P$$

with $\lambda_1 \equiv 2\dfrac{k_2}{k_1}[P]_0 = 3$ and $\lambda \equiv 2\dfrac{k_3[R]_0}{k_1[P]_0} = 98$

[M] taken equal to [P] with efficiency of 1/2 forward and 1 backward, while $[P] \approx [P]_0$

1, inner solution to $0(1/\lambda^2)$; 2, outer solution to $0(1/\lambda^2)$; 3, "far out" solution to $0(1/\lambda)$; 4, Q.S.S.C.

which up to now has been employed throughout the paper for both the "inner" and the "outer" solutions may not under certain conditions be the proper one, in the sense that the coefficients of the perturbations series need not necessarily be restricted to simple powers of $1/\lambda$. A more general approach would consist therefore of representing the appropriate function y as

$$y = \sum_{n=0}^{\infty} f_n(\lambda)\overset{(n)}{y} \quad \text{with} \quad \lim_{\lambda \to \infty} \frac{f_{n+1}}{f_n} = 0$$

in which the unknown functions $f_n(\lambda)$—not necessarily simple powers of $1/\lambda$—would have to be determined from the matching condition between the "outer" and the "inner" solutions. It can easily be shown, of course, that, for the four examples considered in this paper, $f_n = 1/\lambda^n$ but, as has already been observed for certain classical problems in fluid mechanics and heat transfer [7, 8], this simplification may not, in general, always be permissible. Fortunately however, a pleasing and valuable property of the singular perturbation technique is that, in general, the matching requirement cannot be satisfied unless the proper expansion has *a priori* been postulated.

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NOTATION

- C Constants of integration
- C_i Constants of integrations produced by ith perturbation function.
- [I] Concentration of reactive intermediate
- k_i Chemical reaction rate constant for reaction i
- [P] Concentration of product
- [R] Concentration of reactant
- t Dimensional time
- Y_i Dimensionless concentration of species i in the "inner" region
- $\overset{(n)}{Y_i}$ nth order perturbation function for the "inner" solution
- y_i Dimensionless concentration of species i in the "outer" region
- $\overset{(n)}{y_i}$ nth order perturbation function for the "outer" solution
- $\hat{y}_i$ Exact solution for species i
- z_i Dimensionless concentration of species i in the "far out" region
- β Dummy variable of integration
- ϵ Equilibrium departure term
- η Dimensionless time variable for the "far out" region
- λ Perturbation parameter—a dimensionless chemical reaction rate constant
- λ_i Dimensionless chemical reaction rate parameter for reaction i
- τ Dimensionless time
- ω Dimensionless time variable for the "inner" region

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Résumé—L'approximation bien connue de l'état métastable dans l'étude cinétique d'un processus chimique peut être améliorée de façon rigoureuse au moyen d'une technique mathématique: la méthode des perturbations singulières. Les traits essentiels de cette technique sont mis en évidence par l'étude cinétique des 4 processus.

$$R \rightarrow I \rightarrow P; \qquad R \rightleftarrows I \rightleftarrows P$$
$$R \rightarrow I; \qquad 2\,I \rightleftharpoons P$$

et
$$R + M \rightleftharpoons I + P + M; \qquad R + I \rightarrow P$$

Le dernier correspondant au cas de la décomposition thermique de l'ozone.

Zusammenfassung—Es wird gezeigt, dass die bekannte quasi-stationäre Näherungslösung für die Kinetik chemischer Reaktionen ganz beträchtlich verbessert werden kann durch die Methode der "einmaligen Störung".